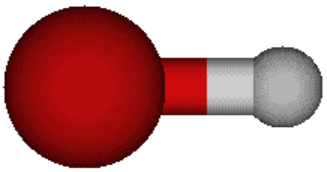
UNIVERSITY OF TEXAS AT AUSTIN– STANTON RESEARCH GROUP

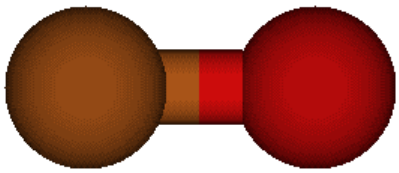
The HOCO System: a Computational Approach

In partial fulfillment of the requirements for graduation with the Dean's Scholars Honors Degree in Physics

Presented by Bert Xue

Spring 2013





_____ _____

John F. Stanton
Supervising Professor

Date

_____ _____

Greg O. Sitz
Honors Advisor in Physics

Date

This thesis work investigates the potential energy surface and kinetic rate of the reaction OH + CO → H + CO2 using computational chemistry. The techniques applied are the High Accuracy Extrapolation ab initio Thermochemistry (HEAT) protocol and the master equation technique in semi-classical transition state theory, which includes quantum tunneling effects. This work is the first theoretical study of the HOCO system to accurately agree with past experimental data at low temperatures, which shows that quantum tunneling is essential for some chemical reactions.

Introduction

The reaction between hydroxide radical (OH) and carbon monoxide (CO) to form free hydrogen radical (H) and carbon dioxide (CO_2) is important in both combustion and atmospheric chemistry. As such, it has been studied extensively both experimentally and theoretically. Previous experimental work has shown that the HOCO system shows non-Arrhenius[i] behavior and strong pressure dependence.[1,2,3,4] In 2010-2011, experimental work on the $HOCO^-$ anion by Johnson et al.[5,6] has shown that the dissociation of the anion into $H^- + CO_2$ occurs below calculated barriers, which suggests that the reaction proceeds through a physical phenomenon known as quantum tunneling. A theoretical study by Li et al.[7] employs a quasi-classical trajectory (QCT) technique on the HOCO system, which agrees with experimental data at temperatures above 1000K, but underestimates the rate below 1000K since it neglects quantum tunneling effects in its calculation. This work, as published by Nguyen et al,[8] shows the importance of quantum tunneling effects in chemical reaction rate calculations.

Background

This work falls under the field of computational thermochemistry, which uses computer programs to calculate important thermochemical data, such as single point energies, transition state geometries, rovibrational constants[ii], and ultimately reaction rate constants, which may be directly compared to experimental data. One of the important uses of computational thermochemistry is that it plays a key role by verifying reaction pathways hypothesized by experimentalists. Low levels of theory can be used to quickly generate simulations and models of complex structures such as proteins. This work uses *ab initio*, which specializes in high accuracy calculation with high levels of theory and detail at the cost of longer computational time, and is generally used on smaller systems of less than 6 heavy atoms[iii].

Ab initio calculations rely on some key quantum mechanical principles. Namely, any physical system[iv] can be fully described by its wavefunction. The goal of the *ab initio* approach is to solve for the wavefunction, thereby allowing the calculation of the physical properties[v] of the system. However, most wavefunctions cannot be derived exactly and must be numerically approximated. This is done computationally by constructing a parameterized basis set[vi] of the wavefunction and optimizing[vii] the parameters to minimize the energy of the wavefunction. Thus, the accuracy of the calculation mainly depends on the basis set used to construct the wavefunction and the level of theory used to calculate the energy of the wavefunction.

Finding the wavefunction through *ab initio* calculations allows us to deduce the energy, rovibrational modes, force gradients along those modes, and many other important physical properties about a system, but this is only a snapshot of a single arrangement in the chemical reaction. Reactions are dynamic, and thus to study chemical reactions a dynamic approach is required: transition state theory.

---

[i] Arrhenius equation: $k = A \exp\left(-\frac{E_a}{RT}\right)$ or $\ln(k) = -\frac{E_a}{R}\frac{1}{T} + \ln(A)$

[ii] Rovibrational constant = analogous to a spring force constant, for rotational and vibrational modes.

[iii] Heavy atoms here refer to non-hydrogen atoms.

[iv] In this case, the physical system is a conglomeration of atomic nuclei and electrons.

[v] Operators (i.e. the Hamiltonian $\hat{\mathcal{H}}$) acting on the wavefuction tells us something about the physical properties of the system (i.e. energy).

[vi] Basis set: the orthogonal vectors (i.e. x^n for power series) that covers the vector space of the wavefunction. Ideally, the basis set covers all degrees of freedom but is normally truncated.

[vii] Theorem: For a given set of boundary conditions, the integral $\langle \Psi^* | \hat{\mathcal{H}} | \Psi \rangle = \bar{E} \geq E_0$. When the expected energy of the system is minimized, the wavefunction corresponds to the ground state.

The essence of the theory is that in order to get from reactants to products, the system must pass through a transition state, generally an excited state whose geometry resembles both the reactant and the product. Properly, the transition state is the saddle point[viii] between the reactants and products. Because the energy of the transition state is higher than the energy of the reactants, the reactants must have enough energy to overcome this energy barrier, which is known as the activation energy. Classically, the reactants have a Boltzmann distribution of energy,[ix] and only the reactants with energy higher than the activation energy can react. This way, the rate of the reaction is dependent on the activation energy, temperature, and the rate of collision between reactants. However, quantum mechanically, systems may have negative kinetic energy, which allows systems with a total energy lower than the activation energy to still go through the transition state, known as quantum tunneling. This work shows the importance of incorporating quantum effects in the calculation of kinetic rate through the addition of a tunneling correction to the classical transition state theory.

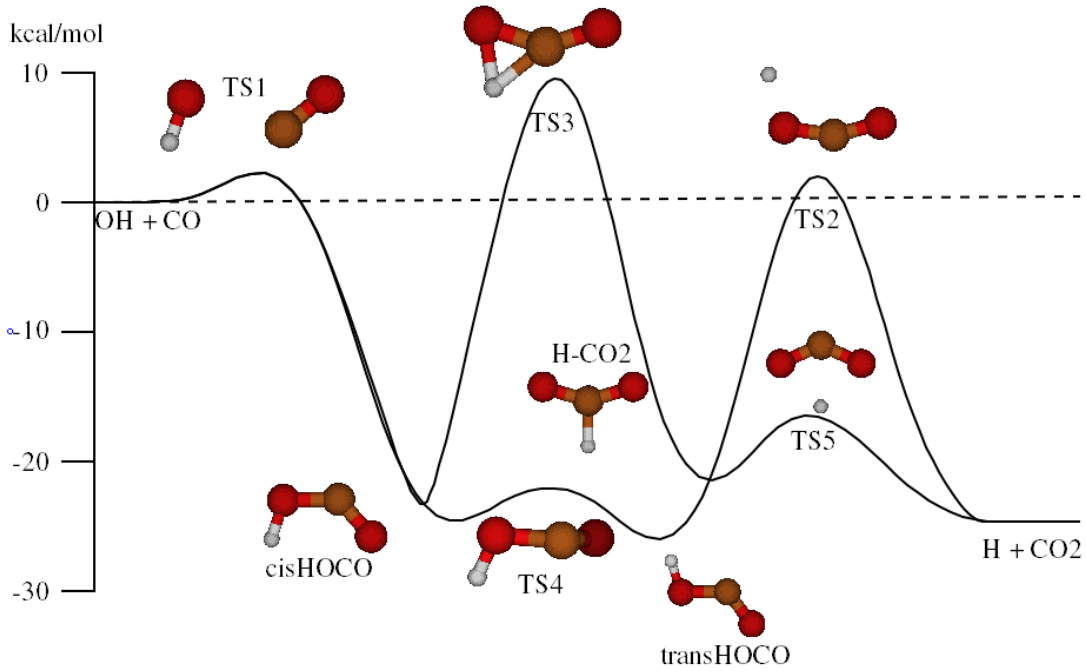


Figure 1: Potential Energy Surface of HOCO System. The x-axis represents the reaction coordinate, and the y-axis represents the energy of the species in kcal/mol. White is hydrogen, brown is carbon, and red is oxygen. Pre-reactive complexes not shown.

The HOCO system starts with the interaction between a hydroxide radical and carbon monoxide. Regardless of the orientation of approach of the pre-reactive complex, the most stable transition state (TS1) leads to the cis-isomer of HOCO. From this point, there are two competing pathways. In the lower-lying path, the cis-HOCO isomerizes through TS4 to trans-HOCO, from which the hydrogen radical can leave the group (TS2) and form carbon dioxide. The other path is the bond shift from the hydrogen and oxygen in cis-HOCO through TS3 to the hydrogen and carbon in H-CO_2. From there, the hydrogen radical can leave the group to form carbon dioxide through TS5.

[viii] At a saddle point, energy is a minimum for most degrees of freedom but a maximum at certain degree(s) of freedom. For a transition state, the maximum is the reaction coordinate.

[ix] proportional to $e^{-E/k_B T}$ where E is energy, k_B is the Boltzmann constant, and T is temperature

Methods

All *ab initio* calculations were done using the CFOUR program package.[9] This calculation makes use of the High Accuracy Extrapolated *ab initio Thermochemistry* (HEAT) protocol set forth by Tajti et al.[10] This protocol is designed to minimize empiricism in the technique, containing only theoretical calculations with empirical extrapolations to complete basis sets. In this protocol, the geometry of each species is first optimized using the CCSD(T)[x] level of at a correlation-consistent basis set of cc-pVQZ[xi]. This process recursively tweaks the configuration of the atoms until the structure corresponds to the minimum or saddle point of the potential energy surface. Then, the single point energy and harmonic frequencies can be calculated. The single point energy is calculated in the form of many terms of varying levels of theory and basis sets, given in the following equation:

$$E_{HEAT} = E_{HF}^{\infty} + \Delta E_{CCSD(T)}^{\infty} + \Delta E_{CCSDT}^{\infty} + \Delta E_{CCSDTQ} + \Delta E_{ZPE} + \Delta E_{DBOC} + \Delta E_{Rel} \qquad \text{(Eq.1)}$$

E_{HF}^{∞} is calculated at the SCF[xii] level of theory with the basis sets of aug-cc-pCVTZ, aug-cc-pCVQZ, and aug-cc-pCV5Z. Values are fit to the function $E_{HF}^{X} = E_{HF}^{\infty} + a * e^{-bX}$ with E_{HF}^{∞}, a, and b as extrapolation parameters.

The next three terms are additions to the energy due to increasing the calculation's level of theory.

$\Delta E_{CCSD(T)}^{\infty}$ is calculated at the CCSD(T) level of theory with the basis sets of aug-cc-pCVQZ, and aug-cc-pCV5Z. Values are fit to the function $E_{CCSD(T)}^{X} = E_{CCSD(T)}^{\infty} + \frac{a}{X^3}$ with $E_{CCSD(T)}^{\infty}$ and a as extrapolation parameters.

$\Delta E_{CCSDT}^{\infty}$ is calculated at the CCSDT(fc) level of theory with the basis sets of aug-cc-pCVQZ, and aug-cc-pCV5Z. Values are fit to the function $E_{CCSDT}^{X} = E_{CCSDT}^{\infty} + \frac{a}{X^3}$ with E_{CCSDT}^{∞} and a as extrapolation parameters.

ΔE_{CCSDTQ} is calculated as a difference between the CCSDTQ(fc) and CCSDT(fc) levels of theory at a basis set of cc-pVDZ.

The last three terms are energy corrections on approximations.

ΔE_{ZPE} is the zero point vibrational energy of the system. It is defined as $\Delta E_{ZPE} = \sum_i \frac{\omega_i}{2} + \sum_{i \geq j} \frac{x_{ij}}{4}$ where ω_i are the harmonic frequencies, x_{ij} are the anharmonicity constants, and i and j are vibrational modes of the system. Harmonic frequencies are calculated at the CCSD(T, fc) level of theory with a basis set ANO2[xiii]. Anharmonicity constants are calculated at the CCSD(T, fc) level of theory with a basis set of ANO1.

ΔE_{DBOC} is the Diagonal Born-Oppenheimer correction. It calculated at the SCF(fc) level of theory with a basis set of aug-pVTZ.

---

[x] CC stands for couple-cluster, and S, D, T, and Q refer to single, double, triple, and quadruple excitation. Parentheses mean a perturbative treatment of that excitation type. (fc) stands for frozen core, meaning interactions with inner shell electrons are neglected.

[xi] aug-cc-pCVXZ is an augmented correlation-consistent basis set (X = D, T, Q, 5, 6, etc.). Some other basis sets have a similar scheme.

[xii] SCF stands for Self-consistent field, using a Hatree-Fock approach

[xiii] ANOx is a basis set that refers to Atomic Natural Orbitals.

ΔE_{Rel} is the energy difference due to a correction to relativistic effects. It is calculated at the CCSD(T) level of theory with a basis set of aug-pCVTZ.

All chemical kinetic rate calculations were done using the MultiWell program package,[11] designed for calculating kinetic rates of reactions with multiple transition states by employing a new semi-classical approach known as the master equation technique.[12] This technique uses energy levels calculated from *ab initio* to create a temperature dependent partition function (Q_x) for each pertinent reactive species and uses rovibrational constants of the transition state(s) to calculate rovibrational cumulative reaction probabilities ($G_x^{\neq}$) which naturally include quantum tunneling factors. Using these quantities, the programs then solve a pressure-dependent master equation to output a kinetic rate given pressure and temperature as parameters. The following equations:

$$k_{P=\infty}(T) = \frac{k_B T}{h} \times \frac{Q_{TS1}^{\neq}}{Q_{HO} Q_{CO}} \times \exp\left(-\frac{\Delta E_{TS1}^{\neq}}{k_B T}\right) \quad \text{(Eq.2)}$$

$$k_{P=0}(T) = \frac{1}{h} \times \frac{Q_{trans,elec}^{\neq}}{Q_{HO} Q_{CO}} \times \sum_{J=0}^{+\infty} (2J+1) \int_0^{+\infty} \frac{G_1^{\neq}(E,J) G_{23}^{\neq}(E,J)}{G_1^{\neq}(E,J) + G_{23}^{\neq}(E,J)} \exp\left(-\frac{E}{k_B T}\right) dE \quad \text{(Eq.3)}$$

represent the high and zero pressure limits of the master equation for the HOCO system, where k(T) is the kinetic rate constant of the reaction, h is Planck's constant, k_B is the Boltzmann constant, T is temperature, E is energy, J is a vibrational quantum number, Q_x are partition functions[xiv], and G_x are the rovibrational cumulative reaction probabilities[xv] of transition state *x*.

In the high pressure limit, molecules constantly collide with the bath gas[xvi], effectively maintaining thermal equilibrium or thermalizing with the system. Thus, any molecule passing through TS1 must thermalize as cis-HOCO before proceeding to the next transition state. In the zero pressure limit, there is no bath gas to thermalize with. Molecules passing through TS1 cannot exchange excess energy as it transitions to cis-HOCO, so energetically the molecule bypasses cis-HOCO and proceeds directly to the next transition state. The kinetic rate obtained from the high and zero pressure limits are then compared to the kinetic rate measured in past experiments.

[xiv] $Q_{trans,elec}^{\neq}$ is the partial partition function of the transition state, combining electronic and translational partition functions.

[xv] $G_{23}^{\neq} = G_2^{\neq} + G_3^{\neq}$

[xvi] Bath gas = the chemically inert gas that is present in the reaction environment, such as He or Ar. Collisions with the bath gas allow the transfer of energy.

Results

Table 1: Single Point Energies (kJ/mol) of HOCO species. Adopted from Nguyen et al.[8] Supporting information of that paper may be consulted for additional data. Species refer to Figure 1.

Species	FCC/CBS	G2M	CBS-QB3	G3	HEAT
HO + CO	0.00	0.00	0.00	0.00	0.00
H + CO_2	-102.88	-103.34	-104.60	-102.51	-103.29
PRC[xvii], OH–CO	-4.07	-7.53			-5.81
PRC, OH–OC	-1.22	-4.18			-0.22
***trans*-HOCO**	-106.03	-100.00	-106.27	-101.67	-103.84
***cis*-HOCO**	-99.02	-93.30	-97.91	-93.72	-97.49
H–CO_2	-41.00	-37.66			-49.31
TS1	2.37	3.35			3.59
TS2	4.31	9.62	4.60		8.16
TS3	35.90	44.77			40.03
TS4	-71.84	-65.27	-72.38	-67.78	-69.62
TS5	-43.31	-39.33			-36.76

Table 1 summarizes the single point energies of the important species in the HOCO system in comparison to previous theoretical work by Yu et al. (FCC/CBS),[13] Zhu et al. (G2M),[14] and Duncan et al. (CBS-QB3 and G3).[15] With the exception of TS5, all other species have energy values calculated through HEAT within a few kJ/mol of the average from other work. This suggests that the HEAT protocol is consistent with past research and theory. Figure 2 shows the total rate of reaction calculated with the high-pressure limit, low-pressure limit, low-pressure limit without tunneling correction, and classical transition state theory in comparison to experimental data by Ravishankara et al.,[1] Golden et al.,[4] Wooldridge et al.,[2] and Fulle et al.[3] Experimental data agree with results from the master equation technique. HO-quenching in Fulle et al.[3] mimics a high pressure environment. The other experiments take place at less than 3 atmospheres, which is considered relatively low pressure. Kinetic rates obtained through SCTST closely model experimental data. Energy values calculated through HEAT are thus consistent with past research, and kinetic rates calculated through SCTST deviate significantly from past theoretical work at low temperatures but model experimental data more accurately than techniques which do not account for quantum effects.

[xvii] PRC stands for pre-reactive complex

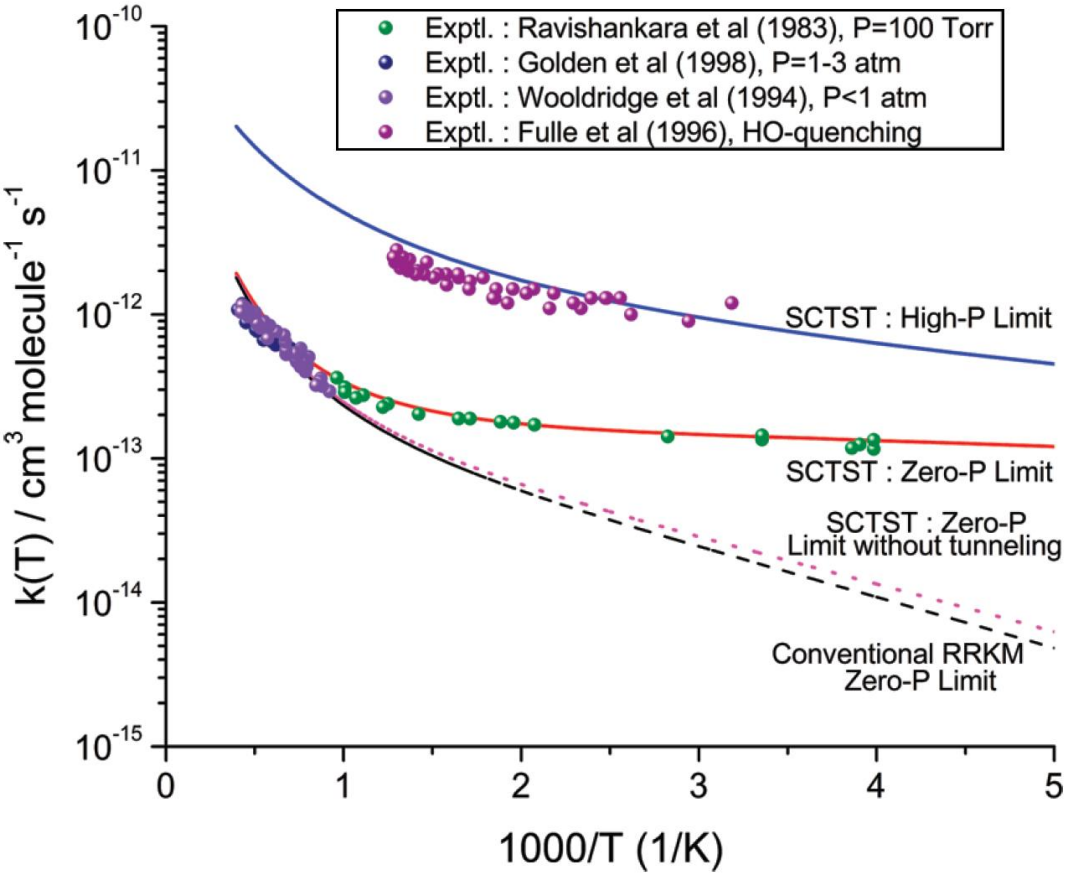


Figure 2: Modified from Nguyen et al.[8] Calculated rates (lines) in comparison to experimental data (points). The x-axis is the inverse temperature, such that lower temperatures are further right and higher temperatures are further left. The y-axis is the rate constant of the bimolecular reaction (in $M^{-1}s^{-1}$) in a logrithmic scale. It is conventional to use the Arrhenius plot because the Arrhenius equation would give a linear plot. RRKM[xviii] theory is the traditional use of classical transition state theory on potential energy surfaces.

Discussion

The main bottleneck for computational thermochemistry is that the amount of computational power needed to do a calculation rises exponentially with the size of the system, the level of theory, and the size of the basis set. Due to limited computational time and storage space, it is not possible to directly calculate the energy of systems at both a high level of theory and a complete basis set. Instead, the HEAT protocol uses extrapolation techniques on larger basis sets at a lower level of theory, while adding corrective terms taken from higher levels of theory at a smaller basis set. This way, the HEAT protocol incorporates both higher levels of theory and large basis sets in the calculation of the energy. This allows for the HEAT protocol to produce accurate values of single point energy while minimizing the amount of empiricism needed in the theoretical calculation.

[xviii] RRKM stands for Rice-Ramsperger-Kassel-Marcus theory, named for the four theorists who contributed to the development of the theory.

One reason why the HOCO system was chosen to be computed in this way is because of its relatively small size. It is computationally less taxing than larger systems simply because there are fewer particles to account for when using *ab initio*. For instance, concurrent work with ketene (CH_2CO) and water (H_2O) to form acetic acid (CH_3COOH) cannot be done using the HEAT protocol within a reasonable amount of time because the system has four heavy atoms as opposed to three. For another reason, there is an ample base of experimental data that may be compared to the results of the calculations because the HOCO system is important in both combustion and atmospheric chemistry. Combustion typically takes place quickly at high temperatures, whereas atmospheric chemistry occurs at low temperature and pressure. Experimental chemists model their experiments with conditions similar to their respective fields, which provide a large temperature range to test this calculation method. Additionally, work by Fulle et al.[16] uses quenching, which mimics a high pressure condition. This allows for a full range of temperature and pressure to compare with the master equation technique.

The main point of this work was to verify the accuracy of the HEAT protocol and demonstrate the need for quantum mechanics in transition state theory. As shown in Figure 2, the chemical kinetic rates at both high and low temperatures agree with the high and zero pressure limit curves calculated from the master equation technique. Neglecting the quantum tunneling terms from equation 3 of the master equation technique shows a decline in rate at low temperatures similar to classical transition state theory. At high temperature[xix], the correction due to quantum tunneling is small because there are a larger proportion of reactants with the energy to pass the barrier height. This is evident as the semi-classical curve and the classical curve converge as temperature increases. However, at low temperature quantum tunneling becomes increasingly important. Even at a temperature of 1000K, the quantum correction term increases the rate of reaction by about 6.5 times, suggesting that more than 85% of the reaction proceeds through quantum tunneling. This factor continues to increases as temperature decreases. It is clear that the experimental data matches the semi-classical approach, strongly suggesting that quantum tunneling is important in certain chemical reactions at low temperatures.

As an interesting aside to the main goal of this work, there is another mode that the hydrogen can leave the H-CO_2 species. As shown in Figure 1, TS5 is the ejection of the hydrogen atom in the direction of the oxygen atoms. As the distance between the hydrogen and the CO_2 increases, the CO_2 relaxes to its linear form. In the other mode, the hydrogen atom is ejected in the opposite direction of the oxygen atoms, which resembles H-CO_2 more closely than TS5. This transition state actually has a lower energy than TS5. The reason that this other transition state was not included in the potential energy surface is because as the hydrogen is removed from the transition state, the electronic configuration of the CO_2 is fixed such that the molecule is bent, with the O-C-O bond angle at roughly 120 degrees. This excited electronic state has a much higher energy than the linear CO_2, and thus is not significant in the reaction.

Conclusion

In this work, *ab initio* calculations were performed following the HEAT protocol to investigate the potential energy surface of the HOCO system. Then, chemical kinetic rate calculations were performed with SCTST to find the kinetic rate constants of the reaction at the high pressure and zero pressure limits. The calculated rates agree well with experimental data between 250K and 2000K. This is the first time that theoretical analysis has calculated the rate of the HOCO system so accurately. Quantum tunneling was found to be essential to the reaction rate, particularly at lower temperatures.

[xix] Temperatures well above 1000K

This work validates the accuracy of both the HEAT protocol and the master equation technique. Small chemical systems should continue to follow the HEAT protocol for high accuracy calculations, and larger systems can use extrapolation techniques from the HEAT protocol at a smaller basis set to achieve similar accuracy within time constraints. Quantum corrections employed by the master equation technique show significant improvement to the accuracy of kinetic rate calculations compared to classical transition state theory. Semi-classical transition state theory should thus be adopted for high accuracy, particularly when quantum effects are suspected to be prominent.

Acknowledgements

I thank the Stanton Research Group, in particular T.L. Nguyen as a close collaborator and J.F. Stanton as the principal investigator and faculty advisor. I would also like to thank G.O. Sitz as another faculty advisor. I thank the Deans Scholars Honors Program in general for the opportunity and environment to be an honors student, in particular D.M. Hillis as the director of DS, and to individual members Andrew Pansick, Steven Stolte II, and Wade Wang for feedback and suggestions in the editing process.

References

[1] Ravishankara, A. R.; Thompson, R. L. *Chem. Phys. Lett.* **1983**, 99, 377.
[2] Wooldridge, M. S.; Hanson, R. K.; Bowman, C. T. In Twenty-Fifty Symposium (International) on Combustion, Irvine, CA, July 31−Aug 5, **1994**; p 741.
[3] Fulle, D.; Hamann, H. F.; Hippler, H.; Troe, J. *J. Chem. Phys.* **1996**, 105, 983.
[4] Golden, D. M.; Smith, G. P.; McEwen, A. B.; Yu, C. L.; Eiteneer, B.; Frenklach, M.; Vaghjiani, G. L.; Ravishankara, A. R.; Tully, F. P. *J. Phys. Chem.* A **1998**, 102, 8598.
[5] Johnson, C. J.; Continetti, R. E. *Phys. Chem. Lett.* **2010**, 1, 1895.
[6] Johnson, C. J.; Poad, B. L. J.; Shen, B. B.; Continetti, R. E. *J. Chem. Phys.* **2011**, 134, 171106.
[7] Li, J.; Wang, Y.; Jiang, B.; Ma, J.; Dawes, R.; Xie, D.; Bowman, J. M.; Gou, H. *J. Chem. Phys.* **2012**, 136, 041103.
[8] Nguyen, T.L.; Xue, B.C.; Weston, R.E., Jr.; Barker, J.R.; Stanton, J.F. *J. Phys. Chem. Lett.* **2012**, 3, 1549-1553
[9] Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G.; Auer, A. A.; Bartlett, R. J.; Benedikt, U.; Berger, C.; Bernholdt, D. E.; Bomble, Y. J.; et al. MOLECULE; Almlöf, J.; Taylor, P. R. PROPS; Taylor, P. R. ABACUS; Helgaker, T.; Jensen, H. J. A.; Jørgensen, P.; Olsen, J. ECP Routines; Mitin, A. V.; van Wüllen, C. *CFour*; **2009**; http://www.cfour.de.
[10] Tajti, A.; Szalay, P. G.; Csaszar, A. G.; Kallay, M.; Gauss, J.; Valeev, E. F.; Flowers, B. A.; Vazquez, J.; Stanton, J. F. *J. Chem. Phys.* **2004**, 121, 11599.
[11] Barker, J. R.; Ortiz, N. F.; Preses, J. M.; Lohr, L. L.; Maranzana, A.; Stimac, P. J.; Nguyen, T. L.; Kumar, T. J. D. *MultiWell Program Suite.* http://aoss.engin.umich.edu/multiwell/ (**2011**).
[12] Weston, R.E., Jr.; Nguyen, T.L.; Stanton, J.F.; Barker, J.R. *J. Phys. Chem. A* **2003**, 117(5), 821-835.
[13] Yu, H. G.; Muckerman, J. T.; Sears, T. J. *Chem. Phys. Lett.* **2001**, 349, 547.
[14] Zhu, R. S.; Diau, E. G. W.; Lin, M. C.; Mebel, A. M. *J. Phys. Chem*. A **2001**, 105, 11249.
[15] Duncan, T. V.; Miller, C. E. *J. Chem. Phys*. **2000**, 113, 5138.
[16] Fulle, D.; Hamann, H. F.; Hippler, H.; Troe, J. J. Chem. Phys. **1996**, 105, 983.